

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 23/08, 27/36, C09D 167/04	A1	(11) International Publication Number: WO 95/15260 (43) International Publication Date: 8 June 1995 (08.06.95)
(21) International Application Number: PCT/GB94/02609 (22) International Filing Date: 29 November 1994 (29.11.94) (30) Priority Data: 9324512.4 30 November 1993 (30.11.93) GB (71) Applicant (for all designated States except US): ZENECA LIMITED [GB/GB]; 15 Stanhope Gate, London W1Y 6LN (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): KEMMISH, John, David [GB/GB]; 96 Dowber Way, Thirsk YO7 1EP (GB). MON-TADOR, James, Henry [GB/GB]; 14 Northpark, Owington Farm, Billingham, Cleveland TS23 3SU (GB). (74) Agents: CHAPMAN, Kenneth, Hazel; Zeneca Bio Products, Intellectual Property Group, P.O. Box 2, Belasis Avenue, Billingham, Cleveland TS23 1YN (GB) et al.		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ). Published <i>With international search report.</i> <i>With amended claims.</i>
(54) Title: BIODEGRADABLE FILM (57) Abstract Biodegradable film comprises at least one layer comprising water-swellaable water-insoluble biodegradable cellulose and/or cellulose acetate and at least one layer comprising crystalline or crystallisable microbiologically produced polyhydroxyalkanoate. Preferably the polyhydroxyalkanoate is R-poly-3-hydroxybutyrate or a copolymer thereof containing 3-20 mol percent of 3-hydroxybutyrate, balance 3-hydroxyvalerate. Composite film may be made by laying the polyhydroxyalkanoate sides of two films together and heat sealing them together.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

BIODEGRADABLE FILM

It is desirable to provide films which are biodegradable. These films which may, for example, become contaminated with food and may be difficult to recycle by conventional means, may be composted so as to reduce their volume and to produce a useful product.

Commonly used biodegradable films comprise cellulose, especially in the form of regenerated cellulose or cellulose acetate. Such films have in general poor barrier properties to water unless the degree of substitution of the cellulose by acetate groups is high, or a layer of a barrier polymer is applied to the cellulose. In either event biodegradability suffers.

This invention comprises biodegradable film comprising at least one layer (hereinafter referred to as the cellulose layer) comprising water swellable water insoluble cellulose or cellulose acetate and at least one layer comprising polyhydroxyalkanoate (PHA).

The PHA is suitably a polymer or copolymer of hydroxybutyric acid, for example a copolymer of (R)3-hydroxybutyric acid with (R)3-hydroxyvaleric acid. Residues of hydroxyvaleric acid may constitute 0 to 25% for example 3 to 20% of the total weight of the polymer. Suitable polymers are disclosed in European Patents 69497 and 52459.

In addition to providing a water vapour barrier, the PHA layer in general also enables the film to be heat sealed to similar sheets and to various other materials if it is a surface layer.

It is preferred that the cellulose layer should comprise regenerated cellulose or should comprise cellulose acetate with a degree of substitution of at most 2.5 and preferably at most 2.3, for example 0.2 to 2.2.

The cellulose layer may be for example 10 to 100 microns thick and the PHA layer 0.5 to 30, for example 1 to 10, microns thick.

Particular examples of the film are: a single cellulose layer and a single PHA layer; two cellulose

layers with a central PHA layer, or two PHA layers and a central cellulose layer.

The film may be produced from pre-formed cellulose film, for example as sold under the trade mark
5 "Cellophane", by applying a layer of the PHA to it and preferably heating to cause the layer to adhere. The PHA may be applied as a solution, for example in a chlorinated solvent for example chloroform. More preferably it is applied as an aqueous suspension,
10 followed by drying. The PHA is preferably to some extent amorphous; (percentage crystallinity typically 0 to 30 for solvent process material, 20-40 for virgin material) then the deposit easily adheres to other materials. If desired, a second cellulose layer may be applied and the
15 result then preferably heated to leave a product in which the PHA layer is sandwiched between two cellulose layers.

If the PHA layer is to be on an outer surface of the film and if the film is to be rolled up soon after formation it is preferred to crystallise the PHA to the
20 extent of typically 40-60% by heating the film, thus rendering the PHA non adhesive.

The liquid solutions or dispersions of the PHA may be applied to the preformed cellulose film in controlled amounts by known means, for example by spreading with a
25 Mayer bar or (preferably) by contacting the film with a gravure roll which is continuously wetted with the liquid, suitably by running a band of film over the top of a rotated gravure roll the bottom of which contacts a reservoir of the liquid.

30 The drying of liquids may be carried out by hot gas heating, e.g. air heating or radiant heating. Solvents other than water are preferably recovered for re-use. It is preferred to use as little solvent or water as possible in order to facilitate drying and to minimise
35 any necessary solvent recovery.

EXAMPLE

Solvent Process

(A) A first latex (A) was produced as follows:
40 40 mL of a 5% (w/v) solution of polyhydroxybutyric acid (PHB) in CHCl_3 is placed in a 400 mL beaker. 200 mL

of 75 mM aqueous hexadecyl (cetyl) trimethylammonium bromide (CTAB) is layered carefully over the PHB solution. The contents of the beaker are then sonicated using a Dawe Soniprobe at maximum power (ca. 200 W) for 5 min using the standard (about ½ in. diameter) horn. To control CHCl₃ release into the air, the operation is carried out either in a fume cupboard or using an ice bath to control excess heating of the sample. The process is repeated until an adequate quantity of emulsion has been prepared. Once prepared the emulsion is stirred magnetically to prevent settling.

Removal of the solvent is then undertaken at the earliest opportunity as follows. 2.25 L batches of fresh emulsion are placed in 5L glass beakers, which are immersed in a 75°C recirculating water bath in a fume cupboard. Each beaker is fitted with an overhead mechanical stirrer. Foaming, which can be quite vigorous, is controllable by adjusting the stirring speed. Solvent removal is allowed to proceed for 8 hr; make-up water may be added as necessary. The final suspension should be odourless and somewhat less opaque than the original emulsion, and is stable indefinitely at room temperature. Precipitation of CTAB will gradually occur. This can be reversed by heating the suspension to 50°C.

Concentration of the particles which result is carried out by centrifugation. On a small scale, this is done conveniently by two rounds of centrifugation, at 10,000 and 40,000g, 30 min each at 20°C. The pellet from each round is resuspended immediately in the desired volume of distilled water. On a larger scale, the suspension can be centrifuged in Beckman centrifuges using the JA.10 (6 x 400 mL) rotors operated at 10,000 rpm (20°C). Under these conditions, partial collection of the particles can be effected by a 1 hr centrifugation; more complete recovery requires longer spin times (> 2hr). Latex A was made up by resuspending particles from the centrifuge in water to produce a suspension containing 21% by weight of solids. The particles are typically 24% crystalline.

(B) A second latex, (B) comprising virgin particles, was made as follows:

Cells of *Alcaligenes eutrophus* were grown in batch culture in an aqueous medium on a mixture of glucose and propionic acid under phosphorus limitation to give a culture containing 160 g/l of cells containing 70% of a 3-hydroxybutyrate (HB)/3-hydroxyvalerate (HV) copolymer with a molar HV content of 4% (the remainder of the polymer being HB).

The cell suspension, which had a dry weight of 160 g/l, was rapidly heated to 150°C by direct injection of steam at 20 bar in a continuous flow steam injector. The cell suspension flowrate was controlled to give a residence time of 80 seconds at 150°C. The cell suspension was then cooled to below 70°C in a continuous flow heat exchanger.

The resulting cell suspension, now at a cell dry weight of 120 g/l due to dilution by condensed steam, was heated to 70°C and the pH raised to 8.0 by addition of NH_4OH solution and the suspension was agitated.

A solution of a proteolytic enzyme sold under the trade name L660 "Optimase", by Solvay, was then added to the cell suspension at a concentration of 0.5% w/w with respect to the cell dry weight. The pH of the suspension was maintained at 8.0 by additions of NH_4OH solution during the 2 hours of the reaction.

At the completion of the reaction, a detergent sold under the trade name "Synperonic" All by Imperial Chemical Industries PLC was added to the suspension at a concentration of 1.0% w/w with respect to the cell dry weight. The pH of the suspension was maintained at 8.0 by addition of NH_4OH solution for 2 hours. The suspension was cooled to below 40°C. The suspended phase, now mainly PHA, was washed by diluting with water and centrifugation three times. The final washed polymer suspension (latex B) had a suspended solids content of 200 g/l. The purity of the individual polymer particles, approximately 1 micron in size and 30% crystalline was typically 96% pure HBHV. The typical composition of the impurities was peptidoglycan 1%; residual protein 2%; and

lipid impurities (methanol soluble 1%).

Film Coating

Regenerated cellulose film 25 μ thick sold under the tradename "Cellophane" was clamped in the sample holder so that it was taut and ripple free. A Mayer bar was placed at the top of the film and the coating material was applied by a Pasteur Pipette to the film in front of the bar. The bar was then drawn down and over the film thus coating it with the latex. The coated film in the sample holder was then placed in an oven at 80°C for 30 seconds to evaporate off the water and form a continuous coating onto the film. The PHA layer was now typically 48% crystalline.

Results

Water vapour transmission rate was measured on 3 replicates of film per sample. Measurements were made via the 'wax-cup' method and used temperate conditions i.e. 25°C/75% Relative Humidity. Results were expressed as g/m²/day.

Coating	Coat Weight g/m ²	WVTR g/m ² /day
None	-	735
Latex A	2.8	152,337,251 Av 210
Latex B	2.1	142,146,152 Av 147

Heat Sealability

2 Pieces of the film were held together with the coated surfaces touching and placed in between the jaws of the heat sealer. The jaws were brought down and the sample was heated for 10 s then allowed to cool for a further 10 s. The jaws were opened and the sample removed.

On inspection the cellulose film had been heat sealed successfully.

CLAIMS

- 1 Biodegradable film comprising at least one layer comprising water-swellaable water-insoluble biodegradable cellulose and/or cellulose acetate and at least one layer comprising crystalline or crystallisable microbiologically produced polyhydroxyalkanoate.
- 2 Film according to Claim 1 in which the polyhydroxyalkanoate is R-poly-3-hydroxybutyrate or a copolymer thereof.
- 3 Film according to Claim 2 in which the polyhydroxyalkanoate contains up to 25, especially 3-20, mol percent of 3-hydroxybutyrate, balance 3-hydroxyvalerate.
- 4 Film according to any one of the preceding claims in which the cellulose layer has a degree of substitution up to 2.5, especially up to 2.3, preferably 0.2 to 2.2.
- 5 Film according to any one of the preceding claims having at least one cellulose layer 10-100 microns thick and at least one polyhydroxyalkanoate layer 0.5 to 30, especially 1 to 10, microns thick.
- 6 Film according to any one of the preceding claims having an outer layer comprising crystallised polyhydroxyalkanoate.
- 7 Composite film comprising two films according to Claim 6 united by heat-sealing their polyhydroxyalkanoate layers together.
- 8 Process for making film according to any one of the preceding claims, said process comprising applying a layer of polyhydroxyalkanoate to preformed cellulose film and heating to cause the applied layer to adhere to the cellulose layer.
- 9 Process according to Claim 8 in which the polyhydroxyalkanoate is applied as an aqueous suspension.
- 10 Process according to Claim 9 in which the polyhydroxyalkanoate suspension as applied comprises virgin particles of 20-40% crystallinity.
- 11 Process according to any one of Claims 3 to 10 in

which the step of heating is sufficient to crystallise the polyhydroxyalkanoate to the extent of 40-60%.

- 12 Process according to any one of Claims 8 to 11 including the further step of laying the polyhydroxyalkanoate sides of two of the films together and heat sealing them together, whereby to make a composite cellulose film.

AMENDED CLAIMS

[received by the International Bureau on 21 April 1995 (21.04.95);
original claims 1,7 and 9 cancelled; original claims 2-6, 8 and
10-12 amended; all claims renumbered 1-9 (1 page)]

1. Process for making biodegradable film comprising at least one layer comprising water swellable water insoluble biodegradable cellulose and/or cellulose acetate and at least one layer comprising crystalline or crystallisable microbiologically produced polyhydroxyalkanoate, said process comprising applying an aqueous suspension of at least partly amorphous particles of polyhydroxyalkanoate to preformed cellulose and/or cellulose acetate film and heating to cause the applied layer to adhere thereto.
2. Process according to claim 1 in which the polyhydroxyalkanoate is R-poly-3-hydroxybutyrate or a copolymer thereof.
3. Process according to claim 2 in which the polyhydroxyalkanoate contains up to 25, especially 3-20, mol percent of 3-hydroxyvalerate, balance 3-hydroxybutyrate.
4. Process according to any one of the preceding claims in which the cellulose and/or cellulose acetate layer has a degree of substitution up to 2.5, especially up to 2.3, preferably 0.2 to 2.2.
5. Process according to any one of the preceding claims in which the product has at least one cellulose and/or cellulose acetate layer 10-100 microns thick and at least one polyhydroxyalkanoate layer 0.5 to 30, especially 1 to 10, microns thick.
6. Process according to any one of the preceding claims in which the product has an outer layer comprising crystallised polyhydroxyalkanoate.
7. Process according to any one of the preceding claims in which the suspension as applied comprises virgin particles of 20-40% crystallinity.
8. Process according to any one of the preceding claims in which the step of heating is sufficient to crystallise the polyhydroxyalkanoate to the extent of 40-60%.
9. Process according to claim 6 including the further step of laying the polyhydroxyalkanoate sides of two product films together and heat sealing them together.

INTERNATIONAL SEARCH REPORT

Internat 1 Application No
PCT/GB 94/02609A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B32B23/08 B32B27/36 C09D167/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B32B C09D C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 534 471 (TOPPAN PRINTING CO., LTD.) 31 March 1993 see page 3, line 7 - line 14; claim 1; table see page 5, line 50 - line 53 ---	1-3,6,7
X	DATABASE WPI Week 9347, Derwent Publications Ltd., London, GB; AN 93-374292 (47) & JP,A,5 278 738 (NISHIKAWA GOMU KOGYO KK) 26 October 1993 see abstract ---	1,2,6
X	DE,A,40 40 158 (PCD PETROCHEMIE DANUBIA DEUTSCHLAND GMBH) 17 June 1992 see claims ---	8,9,12
A	---	1-7
	--- -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

8 February 1995

Date of mailing of the international search report

22.02.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Pamies Olle, S

INTERNATIONAL SEARCH REPORT

Internu 1 Application No

PCT/GB 94/02609

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	EP,A,0 603 876 (BUCK WERKE GMBH & CO) 29 June 1994	1,2,7
P,A	see column 2, line 48 - line 52; claims ---	3,6,8
P,X	DATABASE WPI Week 9445, Derwent Publications Ltd., London, GB; AN 94-363199 (45) & JP,A,6 286 059 (TOPPAN PRINTING CO LTD) 11 October 1994 see abstract ---	1,6
A	EP,A,0 142 950 (IMPERIAL CHEMICAL INDUSTRIES PLC) 29 May 1985 see page 3, line 31 - page 4, line 25 ---	1-7
A	EP,A,0 226 439 (W.R. GRACE & CO.) 24 June 1987 -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/GB 94/02609

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0534471	31-03-93	JP-A- 5245996	24-09-93
DE-A-4040158	17-06-92	NONE	
EP-A-0603876	29-06-94	DE-A- 4244000 PL-A- 301609	30-06-94 27-06-94
EP-A-0142950	29-05-85	AU-B- 576795 AU-A- 3521984 JP-A- 60122527 US-A- 4620999	08-09-88 23-05-85 01-07-85 04-11-86
EP-A-0226439	24-06-87	AU-B- 603076 AU-A- 6601286 DE-A- 3681135 JP-B- 6074340 JP-A- 62209144 US-A- 4826493 US-A- 4880592	08-11-90 11-06-87 02-10-91 21-09-94 14-09-87 02-05-89 14-11-89

